Review Paper

Aluminium-containing scales in water distribution systems: Prevalence and composition

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ABSTRACT

Aluminium (Al) deposits in distribution systems can have important detrimental effects on tap water quality because they can increase turbidity and interfere with disinfection, and they can increase energy loss during water transport. Disruption of the scales could cause the release of associated trace metals. However, there is also the possibility that they have a protective effect on pipe surfaces and thereby reduce metal ion release, assisting with treatment optimization for regulatory compliance. However, relatively little is known about this effect and the composition of these deposits, so little reliable guidance can be given on impacts of treatment changes forced by current and anticipated regulations. In this paper, we summarize what is known about these scales and the sources of the aluminium. We also present new data on the elemental composition of scales found in selected systems in the USA and discuss implications for future study design and important areas of future research that is needed.

Key words | aluminium, aluminium scales, distribution systems, lead pipe scales

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REASONS FOR INTEREST AND CONCERN

Aluminium (Al)-containing scales in water distribution systems are of increasing interest because of their implications in several new areas of regulatory compliance and their impact on distribution system water quality. The stability of such scales and the ability to remove them by changing water chemistry are important relative to the impact of coagulation and corrosion control treatment. One possible beneficial role they can play is that of providing a barrier to corrosion of distribution system materials and to leaching of regulated metals such as lead, or they can provide a substrate to which trace metals might adsorb. Conversely, unpredictable short-term elevations of metal concentrations could result if water quality changes caused them to desorb, or if scale particles were destabilized and released, along with any sorbed or co-precipitated trace metals. Additionally, certain scales cause increased hydraulic friction in the

distribution mains, thereby increasing the energy required to distribute water, and they may function as a sink for corrosion inhibitor chemicals such as phosphates. Many water systems are currently considering upgrading disinfection treatment, removing disinfection byproduct (DBP) precursors, changing coagulants (e.g. alum to a ferric salt), changing coagulant pH and dosage, changing type and concentration of disinfectant, or any combination of these factors. These changes could affect the occurrence, chemical and physical characteristics, and stability of the scales.

The objectives of this study were: (1) comprehensively review the factors that affect Al precipitation in distribution systems; (2) determine the mineralogical and elemental composition of scales from selected distribution systems fed by waters that have been treated using Al coagulants; and (3) obtain corresponding water quality

information and try to ascertain if there are clear relationships to the relative abundance or nature of Al scales in the systems sampled. An understanding of the occurrence and composition of Al scales will enable better control of the chemistry of water treatment and distribution in order to minimize undesirable effects of these deposits, and to take advantage of their protective nature.

SOURCES OF ALUMINIUM IN FINISHED WATER

The presence of Al in water distribution systems can be due to: (1) Al in the source water; (2) Al leached from distribution system materials; and (3) Al introduced to the water from Al-containing coagulants. Al is present in all water supplies (Reiber & Kukull 1996) with concentrations ranging from a few $\mu g \, l^{-1}$ to 2,760 $\mu g \, l^{-1}$ (Kopp 1969; Sollars *et al.* 1989; Van Benschoten & Edzwald 1990*a*; Fuge & Perkins 1991). More than 90% of the Al in most natural water occurs as particulate matter, with the Al bound to colloidal particles or natural organic matter (Reiber & Kukull 1996). Its concentration is usually higher in surface water than in groundwater, especially in areas where water has a low buffering intensity and may have been affected by acid precipitation (Sollars *et al.* 1989; Reijnen *et al.* 1991).

During water treatment, Al salts such as alum are often added to water as coagulants to remove colour, turbidity, particles and natural organic matter (NOM), and these salts affect the Al concentration in the treated water (Letterman & Driscoll 1988; Srinivasan *et al.* 1999). Al concentrations in finished water ranged between 3 and 1,600 $\mu g \, l^{-1}$ (179 $\mu g \, l^{-1}$ average) in a 1969 survey of 380 plants (Kopp 1969), and from 14 to 2,670 $\mu g \, l^{-1}$ (112 $\mu g \, l^{-1}$ average) in a more recent survey (Zimmerman 1986). The residual Al levels vary with factors such as pH (Qureshi & Malmberg 1985), flocculation–filtration effectiveness (Jekel *et al.* 1991), coagulant dosage if it affects pH, NOM concentration (Vik *et al.* 1985), water composition (including turbidity, silica, fluoride and phosphate) and temperature.

Al also may enter water from dissolution of previously precipitated aluminous deposits, cement or asbestos-cement pipes, and exposed cement-mortar linings (primary or relined). Al leaching from cement-mortar linings is especially a problem when the water is low in pH, alkalinity or calcium content (Douglas *et al.* 1996; Bos *et al.* 2000). Soukatchoff *et al.* (2001) observed that aluminium dissolution from cement-based materials in low-alkalinity waters is significantly mitigated by the presence of silica in water. Polyphosphate corrosion inhibitors may increase Al leaching from a cement-mortar liner by attacking and softening cement linings by forming strong soluble chelates with Ca^{2+} and Al^{3+} (LeRoy *et al.* 1996; Berend & Trouwborst 1999). In one of the most extreme cases of aluminium leaching reported, a newly installed cement-mortar-lined pipe was found to increase the Al concentrations from 16 to 550–690 $\mu g \, l^{-1}$ at a kidney dialysis center in Curacao, Netherlands Antilles (Berend & Trouwborst 1999).

TYPES OF ALUMINIUM DEPOSITS AND THEIR EFFECTS

Aluminium deposits form in distribution systems because aluminium particles are not completely removed by filtration, and because the water is supersaturated with solids such as $Al(OH)_{3(am)}$, aluminosilicates, crystalline forms of $Al_2O_{3(s)}$ and aluminium phosphates. Supersaturation leading to Al precipitation may result because of (1) failure to reach equilibrium in the treatment plant during coagulation, flocculation and sedimentation; (2) lowering of temperature during storage and transport; and (3) decreasing pH in the distribution system within the pH range of 6 to 10. Additionally, Al solids may be converted to more crystalline forms of solids that have a lower solubility, or solids that form more slowly and have a lower solubility may precipitate, thereby reducing the concentration of Al that can be in solution at equilibrium. On the pipe surface, the aluminum solid phases may be mixed with other solids such as iron or lead corrosion products, calcium carbonate and manganese dioxide, depending on the composition of the water and the corrosion reactions of pipe material.

Aluminium solubility: pH and temperature effects

It is well known that the solubility and speciation of inorganic aluminium hydroxide strongly depend on

pH (Roberson & Hem 1969; Letterman *et al.* 1999). The minimum solubility of amorphous aluminium hydroxide falls in the pH range of approximately 6.1–6.3 with a soluble aluminium concentration of approximately 20 $\mu g \ l^{-1}$ at 25°C, but at 4°C the point of minimum solubility falls in the range of pH 6.7–6.9, with a soluble aluminium concentration of approximately 4 $\mu g \ l^{-1}$ (van Benschoten & Edzwald 1990*b*). This is in a concentration range and a simple ionic background where only monomeric hydroxo complexes are present. However, certain anions, particularly fluoride when applied before or during coagulation, can increase soluble aluminium levels in this pH range. The pH of minimal solubility can also be changed to values greater than 7, depending on fluoride concentration (Rezania 1985; Feld *et al.* 2000; Pommerenk & Schafran 2002). Many studies have observed significant and sometimes dramatic reductions in soluble aluminium by controlling the pH during coagulation, flocculation, sedimentation and filtration (Zimmerman 1986; Jekel *et al.* 1991). Water temperature during clarification and filtration also is a factor that governs aluminium concentrations in treated water. Anderson *et al.* (1998) calculated that Al solubility at pH 7.9 would range from approximately 20 $\mu g \ l^{-1}$ at 1°C to 430 $\mu g \ l^{-1}$ at 25°C, assuming equilibrium with amorphous $Al(OH)_3$ solid. Since amorphous $Al(OH)_3$ often controls the concentration of Al in filtered water, much higher concentrations of Al are expected at high water temperatures.

Aluminium silicate solids

Silica is an important constituent of most natural waters and is found in combination with Al in many different types of silicate minerals. It is reasonable to investigate whether some of these solids are formed under the conditions that are found in distribution systems. Hem *et al.* (1973) conducted an extensive series of experiments on the effects of silica on the precipitation of aluminium solids from water, and developed a quasi-equilibrium chemical model for a synthetic 'amorphous' aluminosilicate with an Al:Si molar ratio of approximately unity. The presence of even small amounts of silica (2 mg l^{-1} as SiO_2) was seen to considerably slow down the aluminium hydroxide

crystallization process such that crystalline aluminium hydroxide could not be detected by X-ray diffraction (XRD).

Iler (1973) noted that the solubility of silica at pH 8.0 decreased substantially with increasing aluminium solution concentration, which he interpreted as indicating the formation of an aluminosilicate solid that caused a reduction in both aluminium and silica levels. Doucet *et al.* (2001*a*) concluded that the concentration of silicate in natural water is a primary factor in the formation of hydroxyaluminosilicate, which in turn controls aluminium solubility by secondary mineral phase formation. Gallup (1997, 1998) reported that the aluminium-rich amorphous silica scales that were formed at high temperature gave significantly different XRD patterns and crystal morphology from scales that contained crystalline aluminosilicate clays. He observed that aluminium-rich silica scales were a primary precipitate generally deposited from near-neutral, low salinity brines as a non-stoichiometric compound containing approximately 1 Al atom per 7–8 Si atoms. The compound appeared to be aluminium incorporated into an amorphous silica matrix, and could usually be prevented from forming if pH were kept below 5 or above 9.

Gregory & Duan (1998) experimented with the coagulation process and found that dissolved silica could improve, suppress and even prevent coagulation with alum. The mechanism and amount of the effect was found to depend on pH, and they theorized that the effects were a complex function of interactions between the metal ions and dissolved silica, usually related to colloidal charge effects, which modified the hydrolysis species and precipitates. They also observed that silica could be important in affecting the rate of floc formation, and hence the potential for aluminium precipitation, even though the effect on residual turbidity could be negligible. In an extensive review article on silicate complexes of aluminium in water, Swaddle (2001) postulated that ring or cage aluminosilicate anions may be major agents for process surface fouling, because they may act as reservoirs for release of smaller, more reactive units. He noted that direct reactions with aluminium were more prevalent at high pH, and that surface reactions were important in altering hydroxide/oxide crystallization and ageing.

Exley & Birchall (1992, 1993) conducted comprehensive studies of hydroxyaluminosilicate solids in solutions with low aluminium concentrations and pH values relevant to coagulation. The solids were often slow to form, more soluble than aluminium hydroxide, and the silicate prevented the particles from reaching a filterable size. The concentration of silica in the water and the pH of particle formation affected the size and charge distributions of the aluminium particles, and caused them to be different from those normally associated with the hydrolysis of aluminium. The pH representing the minimum solubility and optimal growth and aggregation of particles shifted downwards from about pH 6.5 to 5.5. Their experiments supported the hypotheses that silicic acid either inhibited the nucleation of aluminium hydroxide or inhibited the aggregation of extremely small particles. More recent research has shown the presence of two distinct forms of hydroxyaluminosilicate in natural systems with Si:Al ratios of 0.5 and 1.0 (Doucet *et al.* 2001*a, b*), which were also structurally related to a variety of secondary aluminosilicate species found in soils, such as imogolite, protoimogolite and allophanes. Higher silicate concentration and higher pH of formation favoured the higher Si:Al ratio form. Imogolite can react as follows (Farmer & Lumsdon 1994):

$$0.5 \ (OH)_3Al_2O_3SiOH + 2.5 \ H_2O \leftrightarrow Al(OH)_4^- +$$
$$0.5 \ H_4SiO_4 + H^+; \ K = 10^{-16.7} \text{ at } 25°C$$
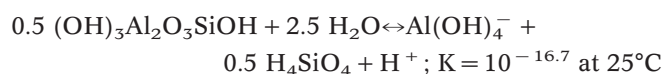
Calculations using this equilibrium constant show alum coagulated waters with silica concentrations as low as 2 mg l^{-1} as SiO$_2$ and 100 μg l^{-1} of Al to be supersaturated with imogolite, and thus highlight the possibility that it could form in drinking water distribution systems. This research provides strong evidence that silica concentration is an extremely important determinant of soluble aluminium concentration in natural systems, and, by logical extension, in treated drinking water.

Aluminium phosphate solids

Interactions between aluminium and phosphate have also been widely reported. This is important relative to distribution system scale occurrence because phosphate corrosion inhibitors for control of lead, copper and iron concentration in tap water are usually applied after filtration and may supersaturate the water with Al-phosphate solids. The precipitate itself may coat pipe walls, thereby causing increased resistance to water flow. The amorphous aluminium hydroxide solid is able to incorporate species like phosphorus into its structure via co-precipitation or by adsorption of orthophosphate onto its surface (Goldberg *et al.* 1996), and cause the formation of more aluminium-containing solid than if the phosphate had not been added. Very little attention has been given to this phenomenon and to the problems that such deposits might cause, in comparison to the benefits of corrosion control and reduced metal release.

The composition of the solid phase that forms depends on the ratio of Al to phosphate concentration and the pH of the water (Goldschmid & Rubin 1988). Although these researchers worked with concentrations of Al and orthophosphate that were much in excess of those encountered in drinking water distribution systems, they showed that at millimolar concentrations in the pH range 7–10, amorphous Al(OH)$_3$ formed and orthophosphate adsorbed to its surface, whereas crystalline aluminium phosphate formed at low pH. The reactivity of the amorphous aluminium hydroxide to phosphate decreases as it ages over the time between 5 and 90 min (Sposito 1989). The decrease in surface reactivity has been attributed to a reduction in the specific surface area of the precipitate owing to its gradual transition from an amorphous solid to a more crystalline aluminium hydroxide (Duffy & van Loon 1994).

Boisvert *et al.* (1997) found similar results when they investigated the adsorption of orthophosphate in the concentration range 0–50 mg l^{-1} onto preformed floc made from alum and from polyaluminium silicate sulfate. A release of OH$^-$ at pH 7 and a release of H$^+$ at pH 5 to 6 accompanied phosphate adsorption. They also showed that when phosphate was present during Al floc formation, substantially more phosphate was incorporated into the floc particle than when the floc was preformed in the absence of phosphate. Further, as phosphate concentration increased, floc size decreased and its zeta potential became more negative. The increase in negative charge was more pronounced as pH increased from 5 to 7.

The interaction of orthophosphate with hydroxy-aluminium polymers was studied by Hsu (1968). The studies covered the pH range from 4.5 to 6 using Al concentrations in the 0.1 to 270 mg l^{-1} range and phosphate-P concentrations in the range 5 to 1,000 mg l^{-1}. The hydroxyaluminium polymers were immediately precipitated by phosphate at their isoelectric points, presumably by simple neutralization of the charge on the polymer by the phosphate anion. The precipitate was X-ray-amorphous and Hsu proposed that it was formed by bridging Al polymers with phosphate ions. Excess phosphate beyond that necessary to form the precipitate was found to replace the OH^- ion in the Al polymer, thus increasing the phosphate content of the precipitate. The reaction could not be described using an equilibrium constant because true equilibrium probably had not been reached, and the approach to equilibrium was too slow to be detected under laboratory conditions.

The results obtained by Hsu (1975) further extend our understanding of the system and are consistent with the formation of an Al-phosphate solid composed of a mixture of Al-O-Al and Al-O-P bonds. The relative amount of these two types of bonds depends on the relative amounts of OH^- and PO_4^{3-}, with Al-O-Al dominating when the amount of PO_4^{3-} is small relative to the amount of Al. The molar ratio of phosphate to aluminium in the precipitate increased to approximately 1:1 as phosphate increased relative to aluminium. Further investigation showed that Al-phosphate solid adsorbed sulfate at relatively low pH where the solid was positively charged, and it adsorbed calcium at higher pH where the solid was negatively charged. Calcium phosphate also precipitated if the concentrations of calcium and phosphate were sufficiently high.

Elemental composition of scales on lead and other pipe

The authors collected scale from each of 10 water utilities as part of this study (see Appendix for experimental procedures and data). This study was conceived as a reconnaissance to determine whether Al-containing solids were prevalent in water distribution system pipes and premise plumbing that could be significant in terms of current or future metal release and stable water quality. The systems were selected based on several factors including: (1) water chemistry; (2) the use of Al coagulants; (3) the use of orthophosphate and polyphosphate inhibitors; and (4) the presence of a large concentration of silica in the water. Additionally, discussions were held with the water quality manager or a similar individual at each plant to determine whether data existed on the hydraulic properties of the pipes, and whether observations had been made which would indicate that deposits had been formed by Al-based deposits. Deposits on lead (Pb) pipes were emphasized first, and deposits on cement, concrete or plastic pipes that might reduce flow second. Deposits on copper (Cu) and unlined cast iron (Fe) samples were given the lowest priority.

The most notable feature of the scale composition data is the large amount of Al, Si and P that is present on lead pipes, in addition to lead (see Table A3). Al is usually present as a large percentage, typically 15 to 70 atom per cent of elements heavier than sodium, whenever Al-based coagulants were used. The percentage is somewhat smaller (2–14 atom per cent) for Lake Bluff and Rochester where PACl was used for coagulation instead of alum. The amount on lead pipes from the New Haven, Connecticut, Saltonstall and Gaillard distribution systems was also relatively small (1–11 atom per cent). The low Al percentages at New Haven might be attributable to the use of polyphosphate as corrosion inhibitor. Potentially the polyphosphate is causing a stable Al particle to form in suspension that does not easily attach to the pipe wall, but further research is required to establish this.

A significant exception to the statement that the use of alum causes large percentages of Al in scales is Columbus, which uses alum but follows coagulation with the lime softening process. The finished water is very low in Al, presumably because the softening process removes Al. The scale sample from Columbus showed a rather large magnesium concentration (26–40 atom per cent) and a high amount of zinc (3–10 atom per cent), the latter being reasonable considering the conversion to zinc orthophosphate treatment at reduced pH for corrosion control in 1980, and observations of hard, apparently zinc silicate deposits on cement pipes (Schock & Buelow 1981; LeRoy

Table 1 │ Summary of published studies documenting investigations of water quality and transport problems associated with aluminium-containing scales in distribution mains and domestic water lines

Study	Observations
Baylis 1953	Reported the rapid build up of a very soft gelatinous coating covering even old tubercles after the South District Filtration Plant was put in operation. It was noted that the piping in many water systems was covered with a white gelatinous coating that was not calcium carbonate. Chemical analysis of the white material showed that it consisted '. . . mainly of aluminium hydroxide, with considerable silica'.
Hudson 1966	When coagulation/filtration operation is improper, aluminium hydroxide can be deposited, regardless of the type of pipe or its lining. Very thin aluminium deposits will materially reduce carrying capacity. Aluminium-containing deposits were reported to substantially decrease C-factors in mains from Chicago.
Cooper & Knowles 1975	More than 40% C-factor reduction for a 42-inch main in the London, Ontario, system within 5 years of installation, caused by an approximately 2 mm thick whitish-grey substance on the internal pipe surface. No coating was observed immediately downstream of the line valve. The material was mostly amorphous interspersed with fine silica, the latter probably derived from the filter media at the treatment plant. Chemical analyses of different samples of deposit ranged from approximately 20–23% Al_2O_3, 25–40% SiO_2, 4–8% CaO, 6–10% MgO, 3–10% Fe_2O_3.
Hoff 1978	Investigation of possible interference to microorganism inactivation by clay and aluminium phosphate particles believed to be representative of particles from some distribution systems.
McGinn & Briggs 1979	Within 2 years of installation of a pumping station, carrying capacity in a 46-inch main was reduced and booster station use increased. Excess headloss was uniform throughout the main. A slimy deposit less than 2 mm thick was found coating the interior. Chemical analysis showed 80–90% aluminium, with small amounts of iron, magnesium, silica and organic carbon. Precipitate buildup was stabilized by polymer replacement and terminating lime feed. Main cleaning by pigging increased Hazen-Williams coefficient from 113 to 139.
Costello 1984	Overview of postprecipitation mechanisms in several water distribution systems, including discussion of 2 Jtu turbidity levels in the Manatee County, Florida, distribution system caused by aluminium coagulation. Aluminium postprecipitation is described as '. . . a serious and widespread problem'.
Qureshi & Malmberg 1985	States that postprecipitation of Al occurs in distribution mains from the Fridley Filtration Plant, Minneapolis, Minnesota.
Anonymous—Onandaga 1985	Thin buildup of aluminium hydroxide sediment was reported in 54-inch main carrying filtered water from the Metropolitan Water Board plant to the Syracuse area. Deposit was rippled and gritty in texture, which could be removed with a rag. A significant loss of carrying capacity was observed. Cleaning raised C factor from 90 to 135.
Anonymous—Lexington 1985	Lexington, Kentucky, reported a reduction of C-factor from 130 to 100 resulting from an approximately 3 mm deposit on the inner wall of 24-inch and 30-inch ID pre-stressed concrete transmission main. Analysis of the metal content of the deposit indicated that 15% of the material was aluminium, with approximately 1.3% calcium. Other metals were less than 1% in concentration. Cleaning via soft pigging restored the original flow and decreased the rate of buildup of the deposit.

et al. 1996). The Columbus results are consistent with the findings of Kvech & Edwards (2002) who reported that Al forms Al-silicate and Al-Mg-silicate solids at pH above 9, thereby reducing the Al solution concentration.

The aluminium-containing deposits may be caused by any of several different water chemistry characteristics. Aluminium residual from the coagulation process can precipitate as Al oxide or hydroxide; as a phosphate

Table 1 │ *Continued*

Study	Observations
Fitch & McCollum 1986	Large doses of alum for coagulation were linked to the rapid loss in transmission capacity, as high as a 2 mgd drop in one large pump. C values were also greatly reduced. A 10 mm maximum thickness gelatinous precipitate was found, composed predominantly of aluminium and silicon oxides.
Zimmerman 1986	Monitoring of turbidity, aluminium, phosphate and some other minor metal levels in the distribution system showed interrelationships with pH and coagulation/filtration trends, indicating Al postprecipitation. When finished water pH was increased, there was evidence of Al solubilization within the distribution system. Increased energy consumption and approximately 25% loss of transmission capacity accompanied the postprecipitation, which reversed when more optimal coagulation conditions were instituted. Studies were also cited where pigging and cleaning or changing coagulants restored transmission capacity lost to thin aluminous deposits in Grand Rapids, Minneapolis, Toronto and Syracuse.
Goold *et al*. 1991	Examination of pipe tap coupons from cement and iron pipe and a section of unlined pipe fed by lime-softened and polyphosphate treated water revealed many common iron minerals and calcium carbonate polymorphs. However, in some of the soft scales considerable organic material was present, along with traces of Cr, Ba, Ni, Sr, Ti, Zn, Mg, Al, P, S and Si.
Fuge *et al*. 1992	Reductions in finished water Al resulting from changes in water sources and treatment in two communities in Wales caused soluble and particulate aluminium remobilization from distribution system network and domestic piping. Particulates from the aluminous deposits sometimes concentrated Pb, Sb, Sn, Cu and Zn.
Shea 1993	Green Bay, Wisconsin, experienced lower than expected water pressures and low C-factors in 36-inch pipelines. A white powder buildup was discovered, which laboratory analysis indicated was aluminium silicate. The addition of an orthophosphate compound did not cause any improvement. After a demonstration project, a comprehensive cleaning programme restored the C-factor from approximately 90–100 to 150.
Lauer & Lohman 1994	After noting aluminium deposition in test pipe rigs, samples from Denver distribution system piping, storage reservoir and lead pipe wall were taken. Analysis indicated 36–42% Al_2O_3, 24–29% SiO_2, 1–3% CaO.
Kriewall *et al*. 1996	Rapid decline in transmission capacity after new filtration plant online.
Kirmeyer *et al*. 1999	Reduction of Pb levels in control loop of pipe rig study fed by this water. Deposit was reddish or reddish-grey in colour with a thickness of about 6 mm. Analysis of the material showed 15% Al and 50% organic matter on a dry basis. The deposit was dissolved and original C-factor was restored by controlling coagulation and post filtration pH.
Havics 2001	Analysis of white precipitates found in municipal drinking water from an unspecified city in Georgia revealed substantial concentrations of aluminium and phosphorus, sometimes associated with Si, Fe and other elements.

precipitate by reaction with corrosion inhibitors that are added after filtration; and as a silicate precipitate by reacting with natural silica or silica that is leached from cement-mortar pipes. The Si percentages were relatively large (5–35 atom per cent), even for utilities such as Lake Bluff, Detroit and Milwaukee, which distributed treated water with only 1.5–2 mg l^{-1} of SiO_2, and were as high as approximately 60 atom per cent at San Luis Obispo where the Si was 15–21 mg l^{-1} as SiO_2. The New Haven silica values were smaller, but the solution silica concentrations

were not available. At least some of the Si is probably combined with Al in the scale, but combination with other metals such as lead, zinc and iron cannot be ruled out based on the analytical procedures available for this study.

The percentages of P were also substantial (2–23 atom per cent) for those utilities that used phosphate inhibitors. The type of inhibitor used included orthophosphate alone, orthophosphate-polyphosphate blends, zinc orthophosphate and a zinc polyphosphate. The analytical methods employed in this study did not allow an overall mass balance, and could not determine the metals to which phosphate is bound, aside from some lead orthophosphate solids that could be identified using X-ray diffraction in some samples (not reported). Whether the form of the phosphate species incorporated into the scale was as orthophosphate or polyphosphate functional groups is also an interesting question, which requires further investigation.

Effects of aluminium scales

Observations of Al-containing solid material of some forms on the walls of distribution system piping have been reported for several decades (see Table 1). As shown, aluminous deposits have repeatedly been implicated as the cause of decreased hydraulic efficiency because of increased roughness and reduced pipe diameter. Besides dramatic decreases in transmission capacity of water mains, Al-containing precipitates in water distribution systems have caused increased turbidity (Srinivasan *et al*. 1999; Kvech & Edwards 2001) and reduced disinfection efficiency (Hoff 1978). Presumably, Al precipitates in the treated finished water can interfere with the disinfection process by enmeshing and protecting microorganisms from disinfection chemicals (Letterman & Driscoll 1988). Zimmerman (1986) noted that the total coliform concentrations in the distribution system decreased after process improvements were made to reduce aluminium residuals. Aluminium-containing deposits such as these, which are similar to those found in soils and sediments, are very likely to be able to accumulate trace metals through sorption or co-precipitation (Schock & Holm 2003). Changes in water chemistry could cause the

release of easily exchangeable trace metal deposits, and thus generate a difficult to detect adverse water quality impact.

Conversely, there is also evidence suggesting that Al-containing solids in the distribution system can play a role in protecting against corrosion or metal ion release to water. Sudden reductions in lead levels during pipe rig testing in a Rochester, New York, case study coincided with the opening of a new filtration plant and appeared to be related to aluminium deposition on Pb piping materials (Kirmeyer *et al*. 1999). This event was also concurrent with the onset of a decrease in transmission main hydraulic capacity specifically identified as being due to aluminium hydroxide deposition (Kriewall *et al*. 1996). Lead concentrations decreased from a range of about 15 to 38 μg l^{-1} to a range of about 5 to 15 μg l^{-1} during the 2.5-month period immediately following Al-based coagulant treatment startup at the Hemlock plant. The lead decrease occurred in spite of either relatively constant or an actual reduction in pH. Analysis of the lead scale material revealed an accumulation of aluminium, in combination with silicon, which was already present prior to coagulation. The buildup was reversed and the original carrying capacity was regained by coagulating at a pH of about 7.6 and then increasing the pH after filtration to about 8.7 during the summer when the Al solubility was the largest (Kriewall *et al*. 1996). The reversibility suggests that at least some of the aluminium analysed in the deposit was there as aluminium hydroxide. Lead levels, however, did not increase when the pH was adjusted to eliminate Al precipitate buildup, suggesting that a thin and protective film of limited reversibility might also have formed to protect against lead release, or that lead release was improved by the higher pH.

Sampling of tap water in the Denver water system to determine compliance with the Safe Drinking Water Act Lead and Copper Rule found that the Pb and Cu concentrations were within acceptable limits. The low Pb levels were surprising considering the treated water pH of 7.4 to 7.8, the alkalinity of 19 to 53 mg l^{-1} as $CaCO_3$ and the negative Langelier Index (-1.6 to -1.0). The pipes were coated with a layer of material whose primary constituents were Al and silicon. The raw water was treated using alum coagulation, flocculation

and sedimentation followed by lime addition for pH control, rapid sand filtration and chlorination. Lauer & Lohman (1994) speculated that the Al-silicate deposit was responsible for the low Pb concentrations and that the rate of deposition was dependent on the Al residual concentration.

Batch corrosion tests of new Pb and Cu pipe segments used water from the Denver Water Moffat treatment plant to examine the potential for forming a protective layer of Al-containing scale (Kvech & Edwards 2001). The Al-silicate deposit was not formed during the test; rather, an attempt was made to coat the pipe surface with particles from deposits taken from the Denver distribution system. No protective effect of the deposit formed in this manner was found. The authors concluded that Al-silicate deposits have mostly negative effects and cannot be recommended for corrosion control. However, the procedure used to develop the scale does not model the conditions under which the deposit was formed in the distribution system, so additional investigation of the effectiveness of Al-silicate deposits is needed.

The Columbus pipe scale showed several interesting characteristics that indicated a protectiveness of the film. While small amounts of crystalline lead solids were detected in the scale, the outer scale layer in contact with the water had a relatively low concentration of lead (5 to 10 atom per cent), but high concentrations of magnesium, silicon, aluminium, phosphorus and zinc as noted previously. Given low levels of lead at the tap, this is consistent with the existence of a protective 'diffusion barrier' kind of scale.

Scale stability

Of concern to the drinking water and public health communities is whether treatment changes can destabilize existing aluminium deposits and, if so, how that destabilization is manifested. One report gives an indication that scales may play a role in determining how metals migrate through a distribution system. High concentrations of lead and copper, and significant increases in tin and zinc concentrations were discovered during sampling of drinking water in a public building with no Pb piping in Wales, UK (Fuge *et al.* 1992). An investigation showed

that the inside of the Cu piping was heavily covered with a green scale. Three samples of the scale contained 68–200 mg kg^{-1} Al, 574–2,940 mg kg^{-1} Pb, 32–112 mg kg^{-1} calcium, 11–273 mg kg^{-1} tin, trace to 5.4 mg kg^{-1} cadmium, 0.4–1.7 mg kg^{-1} antimony, and 52–510 mg kg^{-1} zinc. The elevated Pb levels were attributed to corrosion and re-deposition of lead from solder. The authors found mobilization of the Al-rich pipe encrustations two years after the water treatment system changed from alum to iron salts for coagulation. Unfortunately, the study did not examine the possibility of brass devices as a source of lead, and did not determine the water quality changes that resulted in the scale instability.

CONCLUSIONS

Treatment with aluminium-based coagulants can increase the aluminium concentration in treated water. Measurement of the elemental composition of scales on distribution system piping in several systems that used Al-based coagulants but had different corrosion control approaches showed that substantial amounts of aluminium were present, thus demonstrating that post-precipitation of Al was occurring. An extensive review of the literature showed that Al could form solids consisting of Al oxides, hydroxides, phosphates and silicates. The scale analyses in this study confirmed that aluminium was frequently a major metal in the composition of the scale of lead pipes. The analyses done in this study could not unambiguously determine that these solids are responsible for decreasing the concentration of corrosion products such as lead found at the tap, but circumstantial evidence was developed that make this a plausible hypothesis.

Several previous studies established that post-precipitation of Al is responsible for deposits on inner surfaces of distribution piping that increase the energy required for water transport. Therefore, an important research need is to establish whether Al scales are protective and, if so, how this benefit can be maintained while changing to another coagulant or changing water quality to minimize the adverse effects of such deposits. Alum coagulation may have performance and cost advantages

over other options, so obtaining this information is of critical importance to large numbers of water systems and a large segment of the population.

The composition of the scales raises important questions about the role of the various scale constituents in affecting the concentration of lead in the bulk water. It has been well established that phosphate inhibitors reduce lead concentration in tap water. However, we do not know to what extent aluminium-containing deposits can affect lead solubility or lead release. Most of the lead service line specimens examined in this study showed a complex scale structure with many solid phases containing significant quantities of metals and functional groups (hydroxide, phosphate, silicate) that do not seem to fit simple lead compound passivation models for controlling lead release.

Regardless of whether or not the aluminium scales are significantly protective, evidence from this study suggests that aluminium-containing deposits are at least not universally detrimental towards lead release and compliance with the Action Level under the Lead and Copper Rule. However, it is especially important that more definitive studies be done to show if and when Al solids on lead are protective, which solids are responsible for the best protection against metal release, and which conditions are required to optimize their formation. Further, it is extremely important to ascertain whether water chemistry affects the stability and lead release from Al-containing scales.

The origin of the scale is important, whether or not it is protective or detrimental, because understanding the mechanism of formation will allow proper water treatment adjustments to be made with respect to lead and copper release, corrosivity, and maintenance of distribution system material integrity and optimal hydraulic properties.

Substantial research is also needed to determine the nature of the chemical bonding of aluminium and other constituents in the scale. For example, the elucidation of which metals the phosphate is bound to and whether polyphosphate is included in the scale when it is employed as a corrosion inhibitor is very important, because this information can help enable the best choice of corrosion inhibitor formulation for a given water.

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REFERENCES

Anderson, W. B., Jasim, S. Y., Urfer, D. & Huck, P. M. 1998 Coagulant and pH control alternative for soluble aluminum control. *Proc. Am. Wat. Wks Assoc. Water Quality Technology Conference, San Diego, CA*, 1–4 November.

Anonymous 1985 Onandaga. Pigging cuts power costs in large-diameter water pipe. *Wat. Engng Managmt* **March**, 20.

Anonymous 1985 Lexington. Water main cleanout restores efficient service. *Publ. Wks*, August, 76.

ASTM (American Society for Testing and Materials) 1997 Standard test method for total and dissolved carbon dioxide in water, D 513-92 (Reapproved 1996), Method B (CO_2 Evolution, Coulometric Titration), Conshohocken, PA.

ASTM (American Society for Testing and Materials) 1998 Standard guide for quantitative analysis by energy-dispersive spectroscopy, E 1508-98, Conshohocken, PA.

Baylis, J. R. 1953 Cast-iron pipe coatings and corrosion. *J. Am. Wat. Wks Assoc.* **45**(8), 807.

Berend, K. & Trouwborst, T. 1999 Cement-mortar pipes as a source of aluminum. *J. Am. Wat. Wks Assoc.* **91**(7), 91–100.

Bos, R., Bruins, J. & Rosenthal, L. 2000 Condition management of asbestos cement pipes. *Proc. International Distribution Research Symposium, Denver, Colorado, 10–11 June.* American Water Works Association, Denver, Colorado.

Boisvert, J.-P., To, T. C., Berrak, A. & Jolicoeur, C. 1997 Phosphate adsorption in flocculation processes of aluminium sulphate and poly-aluminium-silicate-sulphate. *Wat. Res.* **31**(8), 1039–1946.

Costello, J. J. 1984 Postprecipitation in distribution systems. *J. Am. Wat. Wks Assoc.* **76**(11), 46.

Cooper, R. E. & Knowles, W. L. 1975 Loss in capacity of a large diameter water pipeline. *Proc. American Water Works Association 95th Annual Conference*, Paper Number 2-3c, Minneapolis, Minnesota, 8–13 June.

Doucet, F. J., Schneider, C., Bones, S. J., Kretchmer, A., Moss, I., Tekely, P. & Exley, C. 2001a The formation of hydroxyaluminosilicates of geochemical and biological significance. *Geochim. Cosmochim. Acta* **15**, 2461.

Doucet, F. J., Rotov, M. E. & Exley, C. 2001b Direct and indirect identification of the formation of hydroxyalumiosilicates in acidic solutions. *J. Inorg. Biochem.* **87**, 71.

Douglas, B. D., Merrill, D. T. & Catlin, J. O. 1996 Water quality deterioration from corrosion of cement-mortar linings. *J. Am. Wat. Wks Assoc.* **88**(7), 99–107.

Duffy, G. W. & Van Loon, S. J. 1994 *Environmental Chemistry*. Oxford University Press.

Exley, C. & Birchall, J. D. 1992 Hydroxyaluminosilicate formation in solutions of low total aluminum concentration. *Polyhedron* **11**(15), 1901.

Exley, C. & Birchall, J. D. 1993 A mechanism of hydroxyaluminosilicate formation. *Polyhedron* **12**(9), 1007.

Farmer, V. C. & Lumsdon, D. G. 1994 An assessment of complex formation between aluminum and silicic acid in acid solutions. *Geochim. Cosmochim. Acta* **58**(16), 3331–3334.

Feld, C. M., Lytle, D. A. & Schock, M. R. 2000 The effect of fluoride on conventional drinking water treatment using aluminum sulfate. *Proc. Am. Wat. Wks Assoc. Water Quality Technology Conference, 5–9 November, Salt Lake City, Utah*.

Fitch, D. E. & McCollum, G. R. 1986 Restoring the flow of a finished water pipeline. *J. Am. Wat. Wks Assoc.,* November, 35–38.

Fuge, R. & Perkins, W. T. 1991 Aluminum and heavy metals in potable waters of the north Ceredigion area, Mid-Wales. *Environ. Geochem. Health* **13**(2), 56–65.

Fuge, R., Pearce, N. J. G. & Perkins, W. T. 1992 Unusual sources of aluminum and heavy metals in potable waters. *Environ. Geochem. Health* **14**(1), 15–18.

Gallup, D. L. 1997 Aluminum silicate scale formation and inhibition: scale characterization and laboratory experiments. *Geothermics* **26**(4), 843.

Gallup, D. L. 1998 Aluminum silicate scale formation and inhibition (2): scale solubilities and laboratory and field inhibition tests. *Geothermics* **27**(4), 485.

Goldberg, S., Davis, J. A. & Hem, J. D. 1996 The surface chemistry of aluminium oxides and hydroxides. Chapter 7 in *The Environmental Chemistry of Aluminium* (Sposito, G., ed.). CRC Press LLC, Florida, USA.

Goldschmid, T. & Rubin, A. J. 1988 Determination of soluble species and precipitates of aluminum phosphate. *Sep. Sci. Technol.* **23**(14, 15), 2269–2291.

Goold, R. R., Wyss, R. G., Horsley, M. B., Elder, D. B., Harms, L. L., Noel, W. F. & Randtke, S. J. 1991 Enhancing distribution system water quality at water district no. 1. *Proc. Am. Wat. Wks Assoc. Water Quality Technology Conference, Philadelphia, Pennsylvania, 23–27 June*.

Gregory, J. & Duan, J. 1998 The effect of dissolved silica on the action of hydrolysing metal coagulants. *Wat. Sci. Technol: Wat. Suppl.* **38**(6), 113.

Havics, A. A. 2001 Two instances of particle contamination in consumer drinking water supplies. *Microscope* **49**(1), 1.

Hem, J. D., Roberson, C. E., Lind, C. J. & Polzer, W. L. 1973 Chemical interactions of aluminum and aqueous silica at 25°C. *US Geological Survey, Water Supply Paper* 1827E.

Hoff, J. C. 1978 The relationship of turbidity to disinfection of potable water. *Evaluation of the Microbiology Standards for Drinking Water*. US Environmental Protection Agency, Washington, DC.

Hsu, P. H. 1968 Interaction between aluminum and phosphate in aqueous solution. *Trace Inorganics in Water*, Advances in Chemistry Series Vol. 73. American Chemical Society, Washington, DC, pp. 115–127.

Hsu, P. H. 1975 Precipitation of phosphate from solution using aluminum. *Wat. Res.* **9**(12), 1155–1161.

Hudson, W. D. 1966 Studies of distribution systems capacity in seven cities. *J. Am. Wat. Wks Assoc.* **58**(2), 157.

Iler, R. K. 1973 Effect of adsorbed alumina on the solubility of amorphous silica in water. *J. Colloid Interface Sci.* **43**(2), 399–408.

Jekel, M. R., Reijnen, G. K., Kostense, A., Verdouw, J., Hiemstra, P. & Peeters, P. G. 1991 Aluminum in water: how can it be removed? Use of aluminum salts in treatment. *Proc. International Water Supply Association, Copenhagen, Denmark, 25–31 May*, pp. SS 8-1–SS 8-4.

Kirmeyer, G. J., Pierson, G., Clement, J., Sandvig, A., Snoeyink, V. L., Kriven, W. & Camper, A. 1999 *Distribution System Water Quality Following Corrosion Control Strategies*. American Water Works Association Research Foundation, Denver, Colorado.

Kopp, J. F. 1969 The occurrence of trace element in water. In: *Proc. 3rd Annual Conference on Trace Substances in Environmental Health,* Hemphill, D.D. (ed.) University Extension Division, University of Missouri, Columbia, Missouri.

Kriewall, D., Harding, R., Naisch, E. & Schantz, L. 1996 The impact of aluminum residual on transmission main capacity. *Publ. Wks* **127**(12), 28–30, 67.

Kvech, S. & Edwards, M. 2001 Role of aluminosilicate deposits in lead and copper corrosion. *J. Am. Wat. Wks Assoc.* **93**(11), 104–112.

Kvech, S. & Edwards, M. 2002 Solubility controls on aluminum in drinking water at relatively low and high pH. *Wat. Res.* **36**, 4356.

Lauer, W. C. & Lohman, S. R. 1994 Non-calcium carbonate protective film lowers lead values. *Proc. American Water Works Association Water Quality Technology Conference, San Francisco, California, 6–10 November*, pp. 1753–1760.

LeRoy, P., Schock, M. R., Wagner, I. & Holtschulte, H. 1996 Cement-based materials. Ch. 7 In: *Internal Corrosion of Water Distribution Systems*, 2nd edn. American Water Works Association Research Foundation/TZW, Denver, Colorado, p. 313.

Letterman, R. D. & Driscoll, C. T. 1988 Survey of residual aluminum in filtered water. *J. Am. Wat. Wks Assoc.* **80**(4), 154–158.

Letterman, R. D., Amirthirajah, A. & O'Melia, C. R. 1999 Chapter 6: Coagulation and Flocculation. *Water Quality and Treatment*, 5th edn. McGraw-Hill.

McGinn, R. A., Jr & Briggs, B. 1979 Line-cleaning 'pig' pays off in energy savings. *Am. City & County*, June, 49.

Pommerenk, P. & Schafran, G. C. 2002 Impacts of prefluoridation on organic matter and particle removal in water treatment. *J. Am. Wat. Wks Assoc.* **94**(2), 99.

Qureshi, N. & Malmberg, R. H. 1985 Reducing aluminum residuals in finished water. *J. Am. Wat. Wks Assoc.* **77**(10), 101–108.

Reiber, S. H., Kukull, W. A. & Standish-Lee, P. 1995 Drinking water aluminum and bioavailability. *J. Am. Wat. Wks Assoc.* **87**(5), 86–100.

Reijnen, G. K., Kostense, A., Verdouw, J. & Hiemstra, P. 1991 Aluminum in groundwater, origin, sampling, analysis, and removal. *Proc. International Water Supply Association, Copenhagen, Denmark, 25–31 May,* pp. SS 8-4–SS 8-8.

Rezania, S. 1985 The occurrence and control of aluminum in drinking waters, doctoral dissertation, University of New Hampshire, Durham, New Hampshire, USA.

Roberson, C. E. & Hem, J. D. 1969 Solubility of aluminum in the presence of hydroxide, fluoride, and sulfate. USGS Water-Suppy Paper 1827-C, US Government Printing Office, Washington, DC.

Schock, M. R. & Buelow, R. W. 1981 The behavior of asbestos-cement pipe under various water quality conditions: Part 2, Theoretical considerations. *J. Am. Wat. Wks Assoc.* **73**(12), 636–651.

Schock, M. R. & Holm, T. R. 2003 Are we monitoring in the right place for inorganics and radionuclides? *J. NEWWA* **117**(2) (in press).

Shea, R. D. 1993 'Pig' cleaning water transmission pipelines. *Publ. Wks,* **June**, 54.

Sollars, C. J., Bragg, S., Simpson, A. M. & Perry, R. 1989 Aluminum in European drinking water. *Environ. Technol. Lett.* **10**, 131–150.

Soukatchoff, P., Baron, J. & Lessirad, L. 2001 Cement-based materials used in drinking water pipe systems. *Wat. Sci. & Technol.: Wat. Suppl.* **1**(4), 227.

Srinivasan, P. T., Viraraghavan, T. & Subramanian, K. S. 1999 Aluminum in drinking water: An overview. *Wat. SA* **25**(1), 47–66.

Swaddle, T. W. 2001 Silicate complexes of aluminum(III) in aqueous systems. *Coordination Chem. Rev.* **October**, 665–686, 219–221.

Van Benschoten, J. E. & Edzwald, J. K. 1990a Measuring aluminum during water treatment: methodology and application. *J. Am. Wat. Wks Assoc.* **82**(5), 71–78.

Van Benschoten, J. E. & Edzwald, J. K. 1990b Chemical aspects of coagulation using aluminum salts-I. Hydrolytic reactions of alum and polyaluminum chloride. *Wat. Res.* **24**(12), 1519–1526.

Vik, E. A., Carlson, D. A., Eikum, A. S. & Gjessing, E. T. 1985 Removing aquatic humus from Norwegian lakes. *J. Am. Wat. Wks Assoc.* **77**(3), 58–66.

Zimmerman, J. A. 1986 Post-precipitation of aluminum. *Proc. AWWA Seminar on Water Quality Concerns in the Distribution System.* American Water Works Association, Denver, Colorado, pp. 41–70.

APPENDIX

Samples of distribution system piping were obtained from ten water utilities throughout the USA. These utilities and the typical composition of their finished water are listed in Table A1, and treatment process information is given in Table A2. Experimental details that were followed appear in the Materials and Methods section below. Table A3 presents elemental composition data for the scales as determined by energy dispersive spectroscopy (EDS) or for total carbonate content (CO_3) by coulometric titrimetry. Except for CO_2, the data are reported as atom per cent of the element for the elements that were analysed (atomic number equal to or greater than 11). Elements with an atomic number less than that of sodium (11) were not determined because of the characteristics of the analytical instrument that was used. Thus, the amounts of hydrogen, oxygen and carbon were not determined by this method. Observations on the data have been integrated into the main body of the paper, above.

MATERIALS AND METHODS

Pipe sample collection procedures

Lead pipe samples were taken from Pb service lines. The selected utilities were asked to have at least two Pb service lines dug up. One 2–3 ft length of sample was cut from each line. Pipe samples were collected in duplicate whenever possible; one set of samples was sent to the Water Supply and Water Resources Division (WSWRD) of the USEPA National Risk Management Research Laboratory in Cincinnati, Ohio, and the other to the University of Illinois at Urbana-Champaign (UIUC). The purpose of duplicate samples was to be able to analyse pipe deposits in two laboratories to confirm the presence of key mineral deposits. Because scale samples in lead and other pipes often display spatial inhomogeneity, seven splits of processed scale sample were made, so that some estimation of analytical performance uncertainty could be developed and separated from what might be sample compositional differences.

Samples of small diameter (2.5–5 cm) pipes were collected, dewatered and capped with a rubber cap so the moisture was retained within the sample, and then shipped. The samples were not shipped full of water

because scale may wash off due to agitation during shipment. Samples of larger pipe with scales that were tightly attached were shipped dry, because they were too large to cap to preserve moisture. These samples were placed in a rigid box so that the scale was not removed by scraping during shipment. If the scale was loosely attached, it was removed and placed in two 100–500 ml clean plastic bottles. Care was taken to avoid including some of the pipe material-of-construction in the sample.

Scale analysis procedures

The solid samples were analysed for water content, total inorganic carbon content, and for elemental content by energy-dispersive spectroscopy (EDS) using the electron microscope. Laboratory procedures and instrumentation differed slightly between the UIUC and WSWRD laboratories. At UIUC, the first step in scale sample processing was to dry the deposit or pipe section under vacuum at ambient temperature. Next, the scales from the pipe surface were removed with the help of a hairbrush or razor blade to differentiate scale layers when possible. The dried material was ground in an alumina/agate mortar and pestle until approximately 98% passed a No. 100 mesh sieve (150-μm diameter). The resulting powder was collected and mixed to achieve as much homogeneity as possible. For the EDS analysis, a small amount of the homogenized powdered sample was mounted on an aluminium stub with the help of double-sided carbon tape, and coated with a thin film of carbon by sputtering. The instrument calibration and quantitative analyses were conducted in accordance with ASTM (1998) Method E1508-98. A Zeiss (Göttingen, Germany) DSM 960 scanning electron microscope fitted with an Oxford Instruments energy dispersive X-ray spectrometer equipped with a beryllium (Be) window and solid-state (SiLi) detector was used for the EDS determinations.

In the WSWRD laboratory, lead pipe samples were first cut longitudinally using a band saw. Cutting debris was removed by laboratory air. The scales were then photographed using a Zeiss Stemi SV11 stereomicroscope at 6 to 66× magnification and 35 mm camera. A section of pipe was kept undisturbed for future reference. Then, scale samples were removed from the cut pipes, first using laboratory brushes of various stiffness to remove outer scale layers when present, then scraping with stainless steel spatulas to remove more adherent under-layers. Depending on scale volume, samples were ground by hand in either synthetic ruby (large) or agate (small) mortars. Whenever practicable, the ground powders were passed through a 200 mesh ($<$75 μm) stainless steel sieve.

For EDS analyses, homogenized splits of the ground powders to be used for XRD and total inorganic carbon (TIC) analyses were made into compressed 7-mm diameter pellets using a stainless steel die set and hand-held 'Quick Press' (International Crystal Laboratories, Garfield, New Jersey). The pellets were mounted on 12-mm diameter aluminium posts with carbon conducting adhesive tabs. The specimens were transferred to a Denton Vacuum DV-502A Evaporative Coater (Denton Vacuum Inc., Cherry Hill, New Jersey) for carbon coating. The specimens were mounted and examined in a JEOL JSM 5800LV scanning electron microscope (JEOL Ltd, Tokyo, Japan) under high vacuum using an Oxford Instruments SiLi detector with a Be window, conjoined with ISIS software. Calibration was conducted on a 99.99% Al standard with ZAF correction applied to all quantitative analysis. Experimentation with geologic and sediment reference materials from NIST (National Institute of Science and Technology, Gaithersburg, Maryland) indicated that the best quantitation was achieved using the software options to not include oxygen and carbon in the analysis or interelemental corrections. As the sample preparation required coating the samples with a layer of graphitized carbon, bias from the carbon coatings was unavoidable, especially in comparison with coulometric TIC analyses. Furthermore, normalization of the total elemental composition to 100% as required by the software can only increase the bias in C from the coating, and that bias would be spread in indeterminable ways throughout the other elements. If elemental composition were reported as weight % of different elements (instead of atom %, as reported in this article), then, theoretically, except for calcium carbonate at 12 wt. % C, probable lead, copper or iron carbonates and hydroxycarbonates would contain only from 3.1 wt. % C (hydrocerussite) to 10.4 wt. % C (siderite). Thus, less bias

Appendix A1 │ Typical water quality of treated water

Location	Utility name	Alkalinity mg l$^{-1(a)}$	pH	Total hardness mg l$^{-1(a)}$	Turbidity NTU	Na mg l^{-1}	Mg mg l^{-1}	Al mg l^{-1}
	Utility Y	100 (raw water)	7.5–8.5	120	0.1	12–14	—	0.1–0.2
	Utility X	99.5–101	7.8–7.9	139	0.14–0.2	7.2	11.1	0.074–0.130
Columbus, OH	Dublin Road	55	7.7	120	0.1–0.2	66–79	6	0.022
	Hap Cremean	26	7.8	129	0.1–0.4	13.6–14	13	0.017
Denver, CO	Moffat	22–28	7.8	36–42	0.06	7.1	2.1	0.02
	Foothills	60–65	7.8	85–101	0.04	19.4	8.5	0.04
	Marston	67–69	7.8–7.9	93–104	0.06	21.4	8.5	0.04
Detroit, MI	Detroit	76	7.4	100	0.44	—	1.2	—
Lake Bluff, IL	CLCWA		—	—	0.1	7.4	—	—
Milwaukee, WI	Linnwood	104	7.5	140	0.22	8.5	—	—
	Howard	100	7.5	140	0.22	8.5	—	—
New Haven, CT	Saltonstall	59	7.2	89.1	0.065–0.08	17.9–20	6.9	—
	West River	16	7.3–7.5	21.5	0.035–0.11	11.2–13	1.7	—
	Lake Gaillard	14	7–7.3	20.6	0.05–0.1	8.3–9	1.8	—
Rochester, NY	Hemlock Lake	63–64	7.7	84–90	0.11–0.18	12–16	6	0.08–0.18
	Lake Ontario	87–89	7.45–7.6	124	0.1	9.5	—	0.1–0.4
San Luis Obispo, CA$^{(c)}$	Before State water added 1997	267	7.7–8	300–350	—	25	37	0.075–0.175
	After State water added	160–230	7.5–8.2	270	0.02–0.05	28	25	0.025–0.2

(a) As CaCO$_3$. (b) Concentration at 90th percentile. (c) In 1998 San Luis Obispo began blending water with California State Project Water.
*11 December 2001 sample.

Appendix A1 │ *Continued*

Si (as SiO$_2$) mg l^{-1}	SO$_4$ mg l^{-1}	Cl mg l^{-1}	Ca mg l^{-1}	Mn mg l^{-1}	Fe mg l^{-1}	Cu mg l$^{-1(b)}$	Pb μg l$^{-1(b)}$	Data Source
—	37	23	35	0.0048	0.048	—	—	Muylwyk, 2001, personal communication
—	27.1–29.1	12.5–14.1	35.1–35.8	—	0.012–0.038	—	—	1999 CCR
8.6	110	40	37	<0.0005	0.08	0.003	<0.5	*
<2.6	80	33	29	0.0006	0.06	<0.002	<0.5	*
6.7–7.4	20.9–25.3	3.1–4.2	14–18	<0.005	0.04	0.196	10	1999 CCR
6.4–7.1	42.7–52.7	17–22.2	26–31.6	<0.005	0.01	0.196	10	1999 CCR
2.8–5.2	46–50.8	19.7–23.6	28.2–31.5	0.013	0.03	0.196	10	1999 CCR
1.5–2.1	23	8.6	28	—	—	—	—	Turner, 2002, personal communication
—	26.3	—	—	—	—	0.12	6.9	Soucie, 2001, personal communication
1.4	27	13	35	0.01	0.02	0.09	12	Couliard, 1999, personal communication
1.5	26	15	36	0.01	0.11	0.09	12	Couliard, 1999, personal communication
—	17.1–42	20.4–37	24.3	—	0.017	0.45	7	1999 CCR
—	8.7–10	17–18.4	5.8	0.03	—	0.45	7	1999 CCR
—	12.3–13.77	7.3–9	5.3	0.01–0.027	0.001–0.012	0.45	7	1999 CCR
—	17–22	21	23–26	0.0026–0.019	—	Nd–0.78	Nd–33	1998 CCR
—	27	22	31–32	0.002	0.04	Nd–0.23	Nd–26	1998 CCR
—	80–140	—	81	—	—	—	—	Fojo, 2000, personal communication
15–21	80	10–22	60–70	—	—	—	—	Fojo, 2000, personal communication

(a) As CaCO$_3$. (b) Concentration at 90th percentile. (c) In 1998 San Luis Obispo began blending water with California State Project Water.
*11 December 2001 sample.

Appendix A2 | Water treatment plant process data

Location	Utility name	Coagulant	Dose (mg l^{-1})	Corrosion inhibitor	Dose (mg l^{-1} as PO$_4$)	Ortho PO$_4$ (mg l^{-1} as PO$_4$)	Poly PO$_4$ (mg l^{-1} as PO$_4$)	Total PO$_4$ (mg l^{-1} as PO$_4$)
—	Utility Y	Alum & Polymer	2–4	No	NA	NA	NA	NA
—	Utility X	Alum & Polymer	8	40% Ortho-PO$_4$ 60% Poly-PO$_4$	0.4 ortho-PO$_4$	0.3	0.2	0.6
Columbus, OH	Dublin Road	Alum	62	Zinc Ortho-PO$_4$ (Zn:PO$_4$ = 1:5)	1.6 ortho-PO$_4$	NA	NA	1.2
	Hap Cremean	Alum	45	Zinc Ortho-PO$_4$ (Zn:PO$_4$ = 1:5)	1.6 ortho-PO$_4$	NA	NA	1.5
Denver, CO	Moffat	Alum & Polymer	NA	No (?)	NA	NA	NA	NA
	Foothills	Alum & Polymer	NA	No (?)	NA	NA	NA	NA
	Marston	Alum & Polymer	NA	No (?)	NA	NA	NA	NA
Detroit, MI	—	Alum	18	H$_3$PO$_4$ Ortho-PO$_4$	1	0.9	NA	0.9
Lake Bluff, IL	CLCWA	PACl	3–4	30% Ortho-PO$_4$ 70% Poly-PO$_4$	0.2–0.3 ortho-PO$_4$	0.3	—	—
Milwaukee, WI	Linnwood	Alum	12	H$_3$PO$_4$ Ortho-PO$_4$	2	1.9	NA	1.9
	Howard	Alum	12	H$_3$PO$_4$ Ortho-PO$_4$	2	1.9	NA	1.9
New Haven, CT	Saltonstall	Alum	NA	Zinc polyphosphate Zn:PO$_4$ = 1:10	(1.1 poly-P as PO$_4$)	—	—	1.2
	West River	Ferric chloride & polymer	NA	Zinc polyphosphate Zn:PO$_4$ = 1:10	(1.1 poly-P as PO$_4$)	—	—	1.4
	Lake Gaillard	Alum & polymer	NA	Zinc polyphosphate Zn:PO$_4$ = 1:10	(1.1 poly-P as PO$_4$)	—	—	1.3
Rochester, NY	Hemlock Lake	PACl & polymer	NA	No	NA	NA	NA	NA
	Lake Ontario	PACl & polymer	NA	No	NA	NA	NA	NA
San Luis Obispo, CA	Blended	Alum & Polymer	—	No	NA	NA	NA	NA
	Pre-blended		—	No	NA	NA	NA	NA

would normally be introduced from excluding C from the normalization than from doing the inter-elemental corrections by including the C from the sample plus coat-

ing. Determination of the oxygen content of the scale samples using EDS is prone to errors as the oxygen Kα peak has to be extracted mathematically from the

Appendix A3 | Scale composition as determined by EDS, including results of interlaboratory comparison. The values from WSWRD laboratory are reported in brackets. All the scales are from lead pipes, unless noted. Concentrations are atom % of elements with atomic number >Na (11) except weight % for CO_2

City	Sample ID	Scale Sample	CO₂	Na	Mg	Al	Si	P	S	Cl	K	Ca	Mn	Fe	Cu	Zn	Pb	Sn
Utility Y	Sample 1*	Entire Scale				60.9	9.0	2.2	2.7	2.5		3.1		17.7	2.0			
	Sample 2**	Entire Scale				68.9	17.7	3.3	1.3	1.3		4.4		2.2				
Utility X	8045 SH	Entire Scale				45.5	18.8	8.1				8.5		4.4			13.9	
	8035 SH	Entire Scale				49.1	21.2	10.0				7.9		6.5			4.8	
	8126 SH	Entire Scale				48.2	19.4	9.5				8.7		3.2			10.1	
	8050 SH	Entire Scale				48.1	15.5	13.8				8.9	1.3	6.9			4.9	
	3345 TS	Entire Scale				37.2	9.6	20.5				11.9	2.7	7.8			10.1	
	3349 TS	Entire Scale				38.4	7.0	18.1				11.3	2.4	6.6			15.6	
	3331 TS	Entire Scale				35.2	7.1	17.0				11.0	2.0	5.5			22.2	
	CDM	1st or Top Layer			1.1	33.6	9.5	22.7			1.0	16.2	1.3	5.7			8.2	
		2nd or Bottom Layer				35.0	5.5	18.5		1.0		11.1		2.3	1.9		23.5	
Columbus, OH	OHCOLA1	1st or Top Layer	1.0		26.2 (39.4)	9.5 (15.4)	34.3 (31.3)	5.3 (4.0)				2.6 (0.9)		1.9 (0.5)		10.0 (3.0)	10.2 (5.5)	
		2nd or Bottom Layer			(2.7)	2.8	4.8	2.3				1.4 (2.3)		1.6	4.1		83.0 (95.0)	
Denver, CO	2828 W. 3rd	Entire Scale				40.5	35.4					3.0		14.5	1.5		5.2	
	4480 Wolf	Entire Scale				44.8	32.9	1.4				4.4		7.7	1.5		7.3	
	685 Emerson	1st or Top Layer				40.7	34.0	1.6				4.2		12.7	1.2		5.6	
		2nd or Bottom Layer				40.0	34.3	1.5				4.0		10.9	1.5		7.9	

Appendix A3 | *Continued*

City	Sample ID	Scale Sample	CO$_2$	Na	Mg	Al	Si	P	S	Cl	K	Ca	Mn	Fe	Cu	Zn	Pb	Sn
Detroit, MI	Sample V-1	1st or Top Layer		3.9		32.4	13.3	6.3			1.0	4.6	14.2	11.6	1.3		11.5	
		2nd or Bottom Layer				22.5	8.4	6.2		7.6		4.0	1.5	1.9			47.8	
	Sample L-1	1st or Top Layer				31.6	12.2	7.2				4.7	12.2	10.7	1.1		19.5	
		2nd or Bottom Layer				24.6	7.5	5.8				2.8		2.2			56.3	
Lake Bluff, IL	ILLB1	1st or Top Layer	6.5		1.7 (1.2)	13.7 (23.8)	21.3 (32.4)	5.0 (5.1)			1.9 (2.1)	7.1 (4.3)		27.5 (16.2)	2.2		19.5 (14.9)	
		2nd or Bottom Layer				5.4 (11.5)	4.7	3.1 (3.7)				4.1 (3.0)		5.5 (1.9)	4.6		72.6 (79.9)	
Milwaukee, WI	Sample 1	1st or Top Layer				21.8	9.1	8.4				5.5		15.6			39.0	
		2nd or Bottom Layer				15.3	5.5	13.3		1.4		6.5		4.3			53.8	
New Haven, CT	CTNHHA1 (a)	1st or Top Layer	2.0			5.3 (7.9)	3.4	21.8 (16.2)				6.7 (3.2)	6.6 (1.2)	34.3 (7.8)	2.1		19.8 (61.0)	(2.7)
		2nd or Bottom Layer	6.2			4.2 (9.0)	2.1	13.5 (16.0)				4.8 (3.3)	1.9	9.7 (4.4)	3.6		60.4 (65.1)	(2.1)
	CTNHYA2 (b)	1st or Top Layer			(1.0)	5.6 (11.2)	1.1 (4.1)	14.8 (26.3)				4.3 (5.6)	21.7 (4.1)	39.1 (25.8)	1.5 (0.6)	4.1 (1.1)	7.8 (20.2)	
		2nd Layer				1.8 (3.5)	2.3	12.7 (17.5)				(1.1)		36.4 (27.7)	3.6		42.6 (50.2)	
		3rd Layer				1.4	1.8	6.7					1.1	23.2	6.3		59.6	
		4th or Bottom Layer	10.6			1.4		4.0						1.5	3.9		89.3 (100)	

Appendix A3 | *Continued*

City	Sample ID	Scale Sample	CO$_2$	Na	Mg	Al	Si	P	S	Cl	K	Ca	Mn	Fe	Cu	Zn	Pb	Sn
New Haven, CT *continued*	CTBFEM3 (a)	1st or Top Layer	3.2			5.7 (11.2)	1.4	22.3 (28.8)				7.7 (7.1)	7.1 (5.4)	35.1 (26.8)	2.2	2.6 (1.6)	16.0 (19.2)	
		2nd or Bottom Layer	8.2			2.6 (5.4)	1.5	16.2 (20.2)				4.3 (3.9)	1.7 (0.9)	18.9 (12.9)	2.7		52.1 (56.7)	
	CTNBHR4 (c)	1st or Top Layer				4.4	2.4	22.2		1.7		3.8	8.2	27.1	2.3	2.9	25.0	
		2nd or Middle Layer				3.0	1.2	15.6		2.1		2.7	11.8	18.0	2.4	2.6	40.7	
		3rd or Bottom Layer				2.9	1.5	18.0		1.5		2.1	2.1	13.2	2.2		56.6	
Rochester, NY	Hemlock	Top Layer	3.0			5.5	17.4	3.8				3.0	2.0	42.0	5.0		21.3	
		Bottom Layer	3.4			1.6	4.7							15.4	6.1		72.2	
San Luis Obispo, CA	Sample Z06***	Entire Scale			2.0	22.3	61.3					12.7						
	Sample Z	1st or Top Layer			2.0	22.5	61.3				1.1	13.1						
		2nd or Bottom Layer			1.9	23.3	59.7	2.1				12.5						

*Scale removed from water meter.
**Scale from plastic pipe.
***Scale from cement-mortar lined pipe.
(a) Saltonstall Treatment Plant.
(b) West River Treatment Plant.
(c) Gaillard Treatment Plant.

collected data by deconvolution of several overlapping peaks of other elements, which may not be feasible because of instrumental resolution constraints. Moreover, the phases present in the scales are expected to contain impurities, and analysing the oxygen content is not meaningful.

Total inorganic carbon was analysed with a UIC, Inc. (Joliet, Illinois) model CM5012 coulometer and model CM5130 acidification module, employing 2% AR-grade $HClO_4$ for digestion and either N_2 or Ar as the carrier gas. The procedure generally followed ASTM D 513-92 Test Method B (ASTM 1997). The measured TIC concentrations for the split samples in this study ranged from 0.1 to 2.9% C, with most under 1%.

Seven splits of samples collected and processed by UIUC were analysed by UIUC and WSWRD; the WSWRD laboratory used different instrumentation in order to gain an estimate of the limits of quantitative uncertainty of the data. The values within the brackets '( )' represent analytical results from the WSWRD laboratory (see Table A3). The results show the variability that can be expected by the two procedures. A comparison of the data for Lake Bluff, Illinois, and New Haven, Connecticut, shows Al values that differ by as much as a factor of approximately 2, and Si data by one procedure of 1 to 4% were not detected by the other procedure, and lead values that differ by as much as a factor of 3. The primary reason for the variability is probably sample inhomogeneity. Small particles of a mineral high in one element may be present in one procedure but not the other, thus causing the variability. In addition, differences could arise due to the scale sampling procedures followed at the two laboratories. Most of the discrepancies between data collected at UIUC and WSWRD is in those samples where multiple layers had been sampled. Sampling different layers, although useful as it gives an idea about the distribution of different elements within the scale, is also subject to errors because of limitations in sampling reproducibility. Therefore, for these samples, we are limited to making conclusions that are based upon general quantities of the elements present, rather than on the specific values that have been determined.